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DEPARTMENT OF ENERGY, MINES AND RESOURCES

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PHYSICAL METALLURGY DIVISION

INTERNAL REPORT PM-R-67-25

DISPERSION-STRENGTHENING OF ZIRCONIUM

PROGRESS REPORT NO. 3

by

C. F. Dixon and H. M. Skelly

Nuclear and Powder Metallurgy Section

December 29, 1967

90-04651/

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SUMMARY OF RESULTS

The work described in this report shows that when thorium oxide (ThO_2) was added to molten zirconium it went into solid solution and precipitated out at the grain boundaries of alpha platelets on cooling. Examination of heat treated specimens of a Zr-2.5% ThO_2 alloy demonstrated that the ThO_2 was soluble in solid zirconium at temperatures of 900°C (1650°F) and above. ThO_2 was also retained in solid solution by water quenching from the molten state. By selective heat treatment, ThO_2 particles about 0.03 micron in size were obtained but the distance between the alpha platelet boundaries on which the ThO_2 precipitated was such that particle spacing was not in the order of a fraction of a micron that is necessary for dispersion-strengthening by blocking of dislocations.

The high-temperature (650°C, 1200°F) tensile strength of the Zr-ThO_2 compositions examined is thought to be due to the ThO_2 particles interfering with recrystallization and grain growth at the testing temperature.

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INTRODUCTION

The work described in this report is part of an investigation being conducted to determine the possibility of improving the high-temperature properties of zirconium for use in nuclear reactors by the addition of refractory compounds to the molten metal. Of the compositions examined, i.e., those containing Y_2O_3, La_2O_3, ThO_2, $CeZrO_4$, $MgZrO_3$, CeO_2 and CeS, the alloys*containing ThO_2 had the highest tensile strength when tested in vacuum at 650°C (1200°F).

Although the presence of thorium is not desirable in alloys used in nuclear reactors, work has been done on Zr-ThO_2 compositions because the high stability of ThO_2 at elevated temperatures afforded the best chance of success. The information obtained will be applied to other zirconium-refractory compositions.

In a previous report[1] it was established that the high-temperature strength of Zr-ThO_2 alloys was not the result of solution in zirconium of either thorium or oxygen arising from decomposition of the ThO_2. In this report, a dispersed-phase present in the Zr-ThO_2 alloys is examined as a possible strengthening medium. Its composition is analysed by X-ray diffraction and the effect of heat treatment on its solubility, size and distribution in a Zr-2.5% ThO_2 alloy is observed. In addition, high-temperature (650°C, 1200°F) tensile properties are determined for heat treated specimens containing 2.5% ThO_2 and the effect of increasing the ThO_2 from 0.7% to 7.0% is also investigated.

ALLOY PREPARATION

The compositions and melt identifications of the alloys referred to in this report are listed in Tables 1 and 2. The materials used to prepare these alloys were reactor-grade zirconium sponge obtained from Carborundum Metals Co. and "purified" thorium oxide powder from Anachemia Chemicals Ltd.

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*Although the zirconium-refractory compositions may not be true alloys they are referred to as such in this report.

The alloys were prepared in a laboratory-size tungsten-arc furnace by striking an arc between the tungsten electrode and the charge contained in a water-cooled copper hearth. An atmosphere of argon at a pressure of 350 mm mercury was maintained during melting.

The zirconium sponge was consolidated by melting into dense material in which a cavity was drilled to contain the ThO_2 powder. The powder was preheated at 800°C (1470°F) for 1 hour then cooled in a vacuum before being added to the zirconium. Each charge weighed approximately 75 grams and was remelted at least four times to ensure homogeneity. The final melting was carried out in a hearth that produced a cigar-shaped ingot.

SPECIMEN PREPARATION AND HEAT TREATMENT

Specimens about 1/4 inch thick, to be used for observation of the dispersed phase, were cut from the cigar-shaped ingots of the Zr-2.5% ThO_2 alloy, then wrapped in tantalum foil and sealed under vacuum in a quartz tube for heat treatment at the temperatures and times shown in Table 1. Part of melt PX was levitation-melted in an argon atmosphere and quenched into water. This specimen was then aged in vacuo at 700°C (1290°F) for 6 hours and water quenched.

For tensile testing, ingots QM and QN(Zr-2.5% ThO_2) were cut in half lengthwise, then each half was wrapped in tantalum foil, sealed in vacuo in quartz and heat treated at 950°C (1740°F) for 6 hours, followed by water quenching. The two heat-treated specimens from melt QM were subsequently hot swaged at 700°C (1290°F) to 0.35 inch diameter rod. Specimens for tensile testing were machined to PMD Drawing No. 115 from the above material and also from ingots containing 3.5%, 5% and 7% ThO_2. Tensile specimens had a total gauge length of 1 inch and a gauge diameter of 0.016 inch.

A specimen for X-ray analysis, 1/8 inch thick, was cut from ingot PX and heat treated at 800°C (1470°F) for 24 hours.

METALLOGRAPHY

Specimens for microexamination were prepared by first rough polishing on silicon carbide abrasive paper to 600 grit. This was followed by polishing with 8 micron and 1/4 micron diamond paste on mirocloth, and then the specimens were chemically polished by swabbing with a solution containing 45 parts

by volume of distilled water, 45 parts by volume of nitric acid and 8 to 10 parts by volume of hydrofluoric acid.

TENSILE TESTS

Tensile tests were carried out at 650°C (1200°F) in a vacuum of 5×10^{-5} mm mercury using an Instron universal testing machine. Each specimen was held at temperature for 1 hour before testing. All tests were carried out in duplicate.

X-RAY ANALYSIS

For X-ray analysis, a G.E. diffractometer with CuK alpha radiation was used.

RESULTS

Effect of Heat Treatment on Microstructure

The photomicrographs at 150 and 1,000 magnifications and the electron micrographs at 5,000 and 30,000 magnifications in Figures 1 to 14 illustrate the effect of heat treatment on the size and distribution of a dispersed phase in the Zr-2.5% ThO_2 alloy. The photomicrographs (Figures 1, 2, 4, 6, 8 and 11) are included mainly to illustrate the general microstructure of the alloys.

The dispersed phase present in these alloys was identified as ThO_2 by X-ray diffraction analysis of a specimen heat treated at 800°C (1470°F) for 24 hours to coalesce the phase (see Figure 5).

Figures 2 and 3 illustrate the ThO_2 precipitated at the alpha-platelet boundaries.

Figure 7 shows that quenching from 900°C (1650°F) results in a re-distribution of the precipitate.

In the specimens heat treated at 950°C (1740°F) and shown in the electron micrographs in Figures 9 and 10, the ThO_2 is almost continuous. The smaller particles in these specimens are in the order of 0.03 micron, whereas the particles in specimens heat treated in a vacuum furnace for 24 hours at 1400°C (2550°F) and furnace cooled (Figure 12) are as large as 3 microns.

The electron micrograph of the specimen water quenched from the molten state (Figure 13) shows little evidence of ThO_2 particles in the microstructure. However, after ageing at 700°C (1290°F) for 6 hours, ThO_2 particles precipitate out of solution, as is shown in the electron micrograph in Figure 14.

Effect of Composition and Heat Treatment on Tensile Properties

The tensile strengths of the Zr-ThO_2 alloys listed in Table 2 are about the same, except for melt QM (Zr-2.5% ThO_2, heat treated and hot swaged), and significantly higher than that of Zircaloy-2.

It is shown above that heat treating the Zr-2.5% ThO_2 alloy at 950°C (1740°F) for 6 hours, followed by water quenching, produces some particles as small as 0.03 micron (see Figure 10); however, this refinement is not reflected in the tensile properties (see melt QN, Table 2).

The results for melts PF (Zr-3.5% ThO_2), PG (Zr-5% ThO_2)and PH(Zr-7% ThO_2 show a decrease in elongation with increasing ThO_2 content.

The results for melts KG and OQ, and Zircaloy-2 are taken from previous reports and included in Table 2 for comparison purposes.

DISCUSSION

The electron micrograph of the Zr-2.5% ThO_2 alloy quenched from the molten state (Figure 13) shows very little precipitate in the structure. This would indicate that the ThO_2 is held in solid solution during quenching and is therefore soluble in molten zirconium. When the Zr-ThO_2 alloys are cooled slower, as in the arc-melted specimens, a precipitate appears at the alpha platelet boundaries as is shown in the photomicrograph in Figure 2 and the electron micrograph in Figure 3.

The X-ray diffraction analysis showed the precipitate to be ThO_2, proving that this compound persists in the zirconium after melting and heat treating. The variation in size and distribution of the ThO_2 with heat treatment indicates that it is soluble in solid zirconium particularly at 900°C (1650°F) and above.

As shown above, refinement of the ThO_2 particles produced no corresponding improvement in tensile strength (cf. Figure 10 and the tensile results for melt QN in Table 2). This lack of response to refinement of the dispersed phase may have been because there was insufficient reduction in the size of the alpha platelets so that the spacing of the ThO_2 particles at the platelet boundaries was not reduced to the order of magnitude required for blocking of dislocation movement.

This work has demonstrated that the Zr-ThO_2 alloys can be heat treated to produce precipitated ThO_2 particles of the size necessary for dispersion-strengthening but the required interparticle spacing has not been obtained.

However, as the results given in Table 2 demonstrate, all the Zr-ThO_2 alloys (except Zr-2.5% ThO_2 heat treated and then swaged) have elevated temperature tensile strengths significantly higher than that of Zircaloy-2. It would appear that in the Zr-ThO_2 alloys examined, the high-temperature strength is due to the ThO_2 particles interfering with recrystallization and grain growth at the testing temperature. Varying the ThO_2 addition from 0.7% to 7.0% resulted in no significant improvement in elevated-temperature strength, indicating that the strengthening is produced by as little as 0.7% ThO_2.

CONCLUSIONS

1. The dispersed phase observed in the Zr-ThO_2 alloys is ThO_2.

2. ThO_2 is soluble in molten zirconium, and in solid zirconium at temperatures of 900°C (1650°F) and above. On cooling, the ThO_2 precipitates at the boundaries of alpha platelets.

3. By selective heat treatment, ThO_2 particles as small as 0.03 micron can be produced.

4. The size of the alpha platelets in all the specimens examined is such that the spacing of the ThO_2 particles at the platelet boundaries is not of the order of a fraction of a micron which is necessary for dispersion-strengthening.

5. There is no significant increase in high-temperature tensile strength on increasing the ThO_2 content from 0.7% to 7.0%.

CFD/HMS/sg

TABLE 1

Heat Treatment of Zr-2.5% ThO_2 Specimens
For Observation of the Dispersed Phase

Melt Ident.	Heat Treatment
PT	As Arc Melted
OQ*	HT 650°C (1200°F) 6hrs, WQ
PX	HT 800°C (1470°F) 24hrs, WQ
PT	HT 900°C (1650°F) 6hrs, WQ
PT	HT 950°C (1740°F) 6hrs, WQ
PT	HT 1400°C (2550°F) 24hrs, Furnace Cooled
PX	Levitation-Melted, WQ
PX	Levitation-Melted, WQ, Aged 700°C(1290°F) 6hrs, WQ

*Reference No. 2
HT - Heat Treated
WQ - Water Quenched

TABLE 2

Heat Treatment and High Temperature (650°C, 1200°F)
Tensile Properties of Zr-ThO_2 Alloys

Melt Ident.	Nominal Composition	Heat Treatment	UTS (kpsi)	0.2% YS (kpsi)	% El. on 1 in.
KG*	Zr-0.7% ThO_2	Hot Swaged, HT 700°C(1290°F) 6 hrs, WQ	23.6	14.7	48
OQ**	Zr-2.5% ThO_2	HT 650°C(1200°F) 6 hrs, WQ	26.1	17.5	22
QN	Zr-2.5% ThO_2	HT 950°C(1740°F) 6 hrs, WQ	23.7	16.5	27
QM	Zr-2.5% ThO_2	HT 950°C(1740°F) 6 hrs, WQ, Hot Swaged	18.2	11.7	52
PF	Zr-3.5% ThO_2	As Arc-Melted	27.0	17.3	35
PG	Zr-5% ThO_2	As Arc-Melted	26.6	17.6	26
PH	Zr-7% ThO_2	As Arc-Melted	25.5	16.3	20
-	Zircaloy-2*	As-Received	17.0	11.9	21

*Reference No. 1. **Reference No. 2
HT - Heat Treated
WQ - Water Quenched

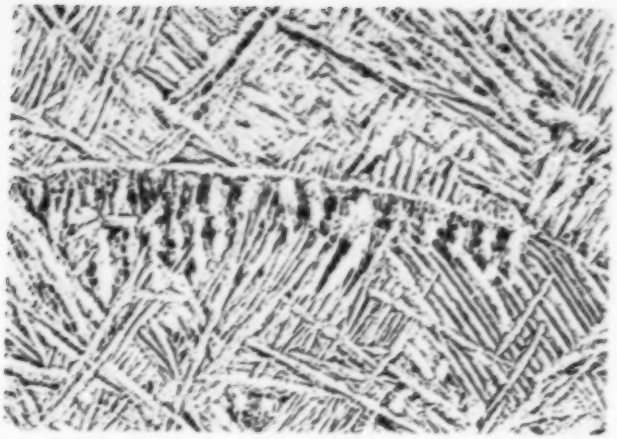
ACKNOWLEDGEMENTS

The authors wish to thank Miss Joyce Ng-Yelim for assistance in obtaining the electron micrographs and Dr. C. M. Mitchell for the X-ray diffraction analysis, both of the Metal Physics Section, Physical Metallurgy Division.

REFERENCES

1. C. F. Dixon and H. M. Skelly - "Dispersion-Strengthening of Zirconium. Progress Report No. 1" - Mines Branch Investigation Report IR 65-76. Department of Mines and Technical Surveys, Ottawa (Sept. 20, 1965).

2. C. F. Dixon and H. M. Skelly - "Dispersion-Strengthening of Zirconium. Progress Report No. 2" - Physical Metallurgy Division Internal Report PM-R-66-15, Mines Branch, Department of Energy, Mines and Resources, Ottawa (July 28, 1966).



X150

Figure 1. Zr-2.5% ThO_2, Melt PT. As Arc-Melted. Chemical Polish.

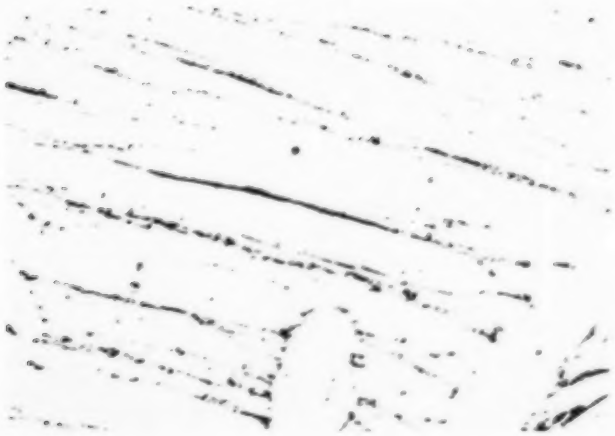


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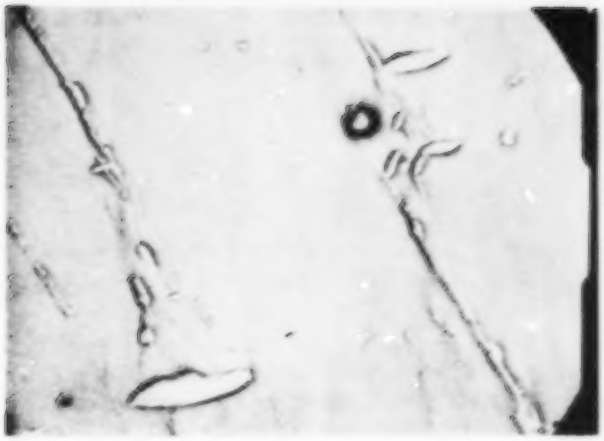
Figure 2. Zr-2.5% ThO_2, Melt PT. As Arc-Melted. Chemical Polish.



X5,000

Figure 3. Zr-2.5% ThO_2, Melt PT. As Arc-Melted. Chemical Polish

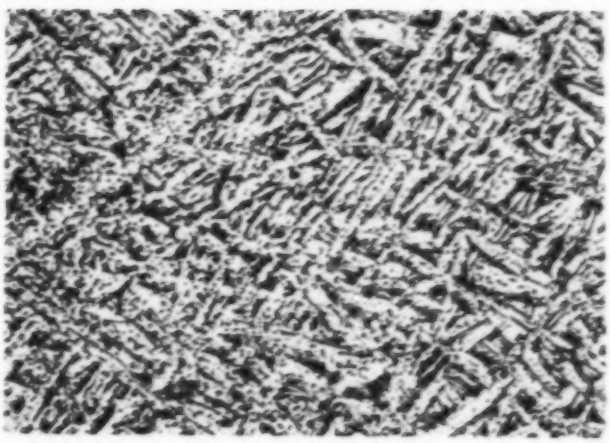


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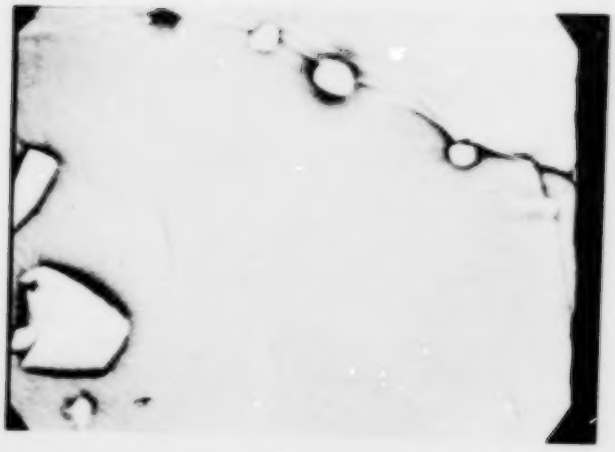
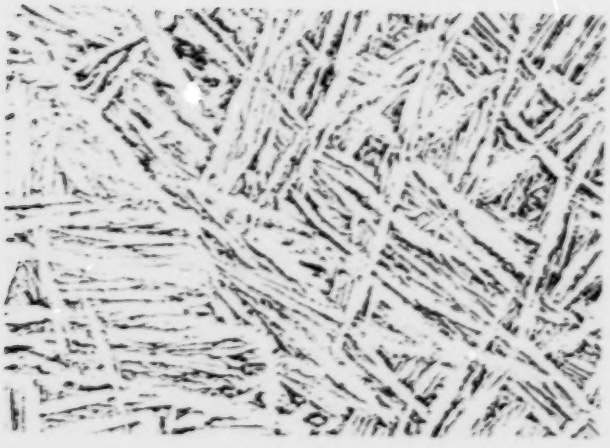
Figure 4. Zr-2.5% ThO_2, Melt PX. HT 800°C (1470°F) 24hrs,WQ. Chemical Polish.



X5,000

Figure 5. Zr-2.5% ThO_2, Melt PX. HT 800°C (1470°F) 24hrs,WQ. Chemical Polish.

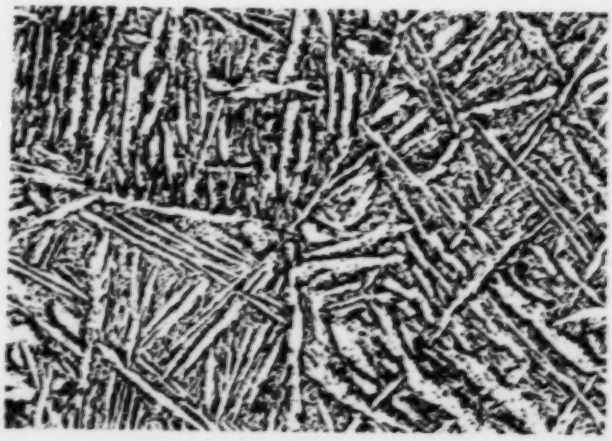


X150

Figure 6. Zr-2.5% ThO_2, Melt PT. HT 900°C (1650°F) 6hrs,WQ. Chemical Polish.

X5,000

Figure 7. Zr-2.5% ThO_2, Melt PT. HT 900°C (1650°F) 6 hrs, WQ. Chemical Polish.

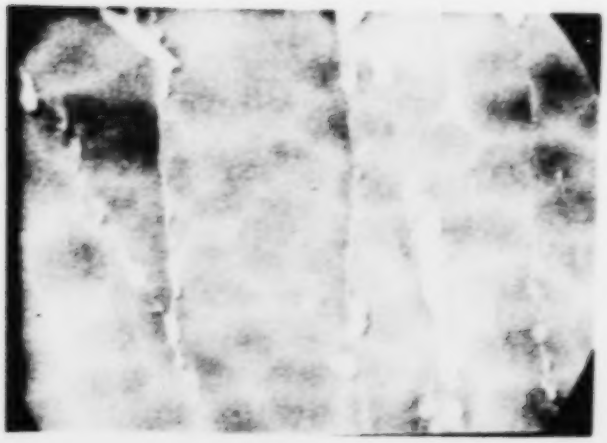


X150

Figure 8. Zr-2.5% ThO_2, Melt PT. HT 950°C (1740°F) 6 hrs, WQ. Chemical Polish.

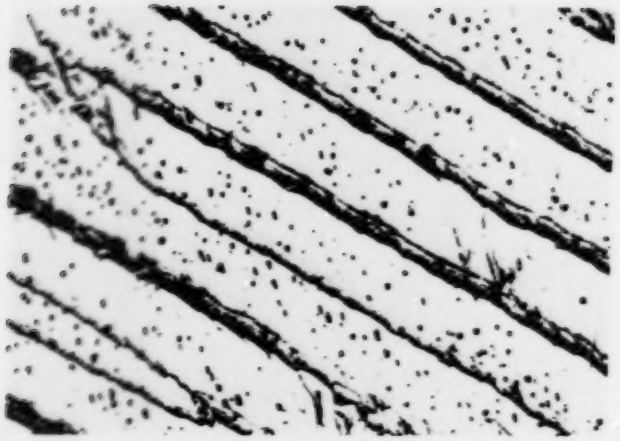
X5,000

Figure 9. Zr-2.5% ThO_2, Melt PT. HT 950°C (1740°F) 6 hrs,WQ. Chemical Polish.



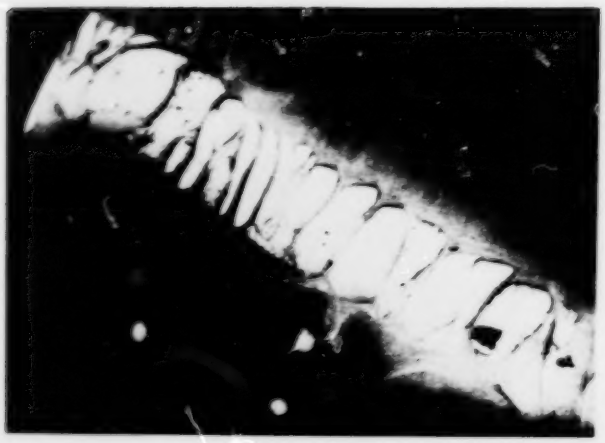
X30,000

Figure 10. Zr-2.5% ThO_2, Melt PT. HT 950°C (1740°F) 6 hrs,WQ. Chemical Polish.



X150

Figure 11. Zr-2.5% ThO_2, Melt PT. HT 1400°C (2550°F) 24 hrs. Chemical Polish.



X5,000

Figure 12. Zr-2.5% ThO_2, Melt PT. HT 1400°C (2550°F) 24 hrs. Chemical Polish.

X5,000

Figure 13. Zr-2.5% ThO_2, Melt PX. Levitation-Melted WQ. Chemical Polish.

X5,000

Figure 14. Zr-2.5% ThO_2, Melt PX. Levitation-Melted WQ. Aged 700°C (1290°F) 6 hrs. Chemical Polish.